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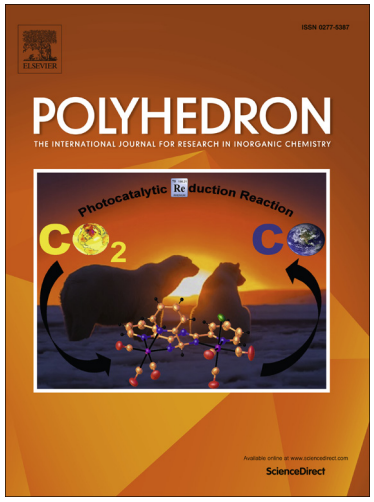

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Dimeric nickel(II) and copper(II) complexes of the pentadentate N_3S_2 chelating agents derived from S-alkyl/aryl esters of dithiocarbazic acid

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ABSTRACT

The helical dimeric copper(II) complex $[Cu(dapsbz)]_2$ (dapsbz = doubly deprotonated form of the 2,6-diacetylpyridine Schiff base of S-benzyldithiocarbazate) has been synthesized and structurally characterized. Each Schiff base in the dimer acts as a doubly negatively charged N_3S_2 pentadentate chelating agent, providing three donor atoms, *viz*. the pyridine nitrogen atom, the azomethine nitrogen atom and the thiolate sulfur atom, to one copper ion and the azomethine nitrogen atom and thiolate sulfur atom to the second copper(II) ion. The stereochemistry adopted by each copper(II) ion in the dimer is five-coordinate, approximately square-pyramidal, with a CuN_3S_2 coordination core. In the dimeric nickel(II) complex, $[Ni(dapsme)]_2$ (dapsme = doubly deprotonated form of the 2,6-diacetylpyridine Schiff base of S-methyldithiocarbazate), the Schiff bases also coordinate with the two nickel(II) ions as pentadentate N_3S_2 chelating agents, but here the pyridine nitrogen atom of each ligand acts as a bridging donor atom. The azomethine

nitrogen and thiolate sulfur atoms of one arm of a ligand coordinate with one nickel ion whereas the azomethine nitrogen and thiolate sulfur atoms of the other arm of the same ligand coordinate with a second nickel atom, the stereochemistry adopted by each nickel atom in the dimer being distorted octahedral with a NiN_4S_2 coordination sphere.

Keywords:

2,6-Diacetylpyridine Schiff bases of S-methyl- and S-benzyldithiocarbazate; Nickel(II) and copper(II) complexes; Pentadentate N_3S_2 chelating agents; dithiocarbazates.

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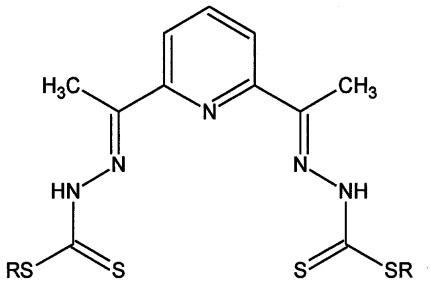
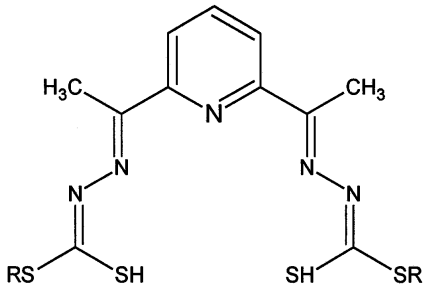
1. Introduction

Schiff bases formed by the condensation of S-alkyl/aryl esters of dithiocarbazic acid with heterocyclic aldehydes and ketones and their metal complexes have been the subject of a large number of studies [1-9], mainly because of their interesting physical and chemical properties [10-13] and potentially useful biological activities [14-27]. However, in the past, most studies on metal complexes of Schiff bases derived from S-alkyl/aryl esters of dithiocarbazic acid have been concerned with complexes of bi- and tridentate chelating agents. Pentadentate dithiocarbazate ligands have received less attention, perhaps due to the scarcity of transition metals that can

accommodate a pentagonal planar array of donor atoms. We have previously found that the pentadentate chelating agent formed by the condensation of 2,6-diacetylpyridine with S-benzyldithiocarbazate (Fig. 1a, R = $CH_2C_6H_5$; H_2dapsbz) yields an unusual pyridine nitrogen-bridged dimeric nickel(II) complex [1e].



(1a ; R = CH_3 , -$CH_2C_6H_5$; thione form)



(1b ; thiol form; R = CH_3 , $CH_2C_6H_5$)

The Schiff base has also been found to form a dimeric zinc(II) complex [1f], but the mode of its bonding with the zinc(II) ions has been found to be different from that with the nickel(II) ion. The Schiff base formed from 2,6-diacetylpyridine and S-methyldithiocarbazate (Fig. 1a; R = CH_3; H_2dapsme) has also been found to act as a pentadentate N_3S_2 ligand, yielding seven-coordinate pentagonal bi-pyramidal tin(IV) complexes [1g]. The preparation and spectroscopic characterization of the nickel(II) complex of H_2dapsme have been previously

reported [27] and based on available evidences, a monomeric six-coordinate octahedral structure was predicted, though crystallographic structural work to establish its structure unequivocally has not been done. The complex $[Cu(dapsbz)]_2$, however, is new and has not been reported previously.

In view of the different modes of coordination of pentadentate chelating agents derived from S-alkyl/aryl dithiocarbazates and the interesting structural features and biological activities of their metal complexes, we report here the preparation and X-ray structures of double helical di-Cu(II) and di-Ni(II) complexes of the 2,6-diacetylpyridine Schiff bases of S-benzyl- and S-methyldithiocarbazate, respectively.

2. Experimental

2.1 Reagents

All the chemicals and solvents used in the present work were of analytical reagent grade and used without any further purification.

2.2 Physical measurements

The electronic spectra were recorded on a Shimadzu UV-3100 spectrophotometer. The IR spectra were recorded on a Perkin-Elmer 1600 FT IR spectrometer. All other physical measurements were performed as described previously [1g].

2.3 Synthesis of the compounds

The Schiff bases H_2dapsme and H_2dapsbz were prepared following procedures described previously [1f, 27].

2.3.1 Preparation of [Ni_2(dapsme)$_2$]

A solution of nickel(II) acetate tetrahydrate (0.30 g, 1.1 mmol) in a hot 1:1 mixture (100 mL) of ethanol and 2,2-dimethoxypropane was mixed with a boiling solution of the ligand H_2dapsme (0.60 g, 1.1 mmol) in a 1:1 mixture (400 mL) of abs. ethanol and 2,2-dimethoxypropane. The resulting mixture was heated on a water bath for 15 minutes and then left to stand overnight at room temperature, whereupon brown crystals of the complex were formed which were filtered off, washed with cold absolute ethanol and dried *in vacuo*. Yield: 0.23 g (50%). Calcd. for $C_{13}H_{15}N_5S_4Ni$: C, 36.46; H, 3.53; N, 16.35. Found: C, 36.15; H, 3.83; N, 16.69 % . Λ (ohm^{-1} cm^2 mol^{-1}, dmso): 8.0. IR (cm^{-1}): 1593m (νC=N); 1082m (νN-N); 949s, 980sh (νCSS). UV-Vis (λ_{max}/nm, dmf): *ca*. 640sh, 420sh, 348, 323.

2.3.2 Preparation of [Cu(dapsbz)]$_2$

The Schiff base H_2dapsbz (0.60 g, 1.2 mmol) was dissolved in a boiling 1:1 mixture (300 mL) of acetonitrile and 2,2-dimethoxypropane to give a bright yellow solution. A solution of copper(II) acetate monohydrate (0.24 g, 1.2 mmol) in a hot 1:1 mixture (100 mL) of absolute ethanol and 2,2,-dimethoxypropane was added and the mixture was heated, with stirring, on a water bath for about 15 minutes, then it was left to stand overnight. The dark green crystals that formed were then filtered off, washed with cold abs. ethanol and dried in a vacuum desiccator over anhydrous silica gel. Crystals of the complex suitable for X-ray diffraction were obtained by recrystallizing the compound from acetonitrile. Yield: 0.363 g (61%). Found: C, 51.05; H,

4.20; N, 11.80. Calcd. for $C_{50}H_{46}N_{10}S_8Cu_2$: C, 51.30; H, 3.96; N, 11.97 %. Λ (ohm^{-1} cm^2 mol^{-1}, dmso): 10.1. IR (cm^{-1}): 1571m (νC=N); 1120m (νN-N); 1035s, 1010sh (νCSS). UV-VIS (λ_{max}/nm, dmf): *ca.* 600sh, 425, 346.

2.4 Crystal structure determination and refinement

Cell constants for $[Ni_2(dapsme)_2]$ were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured on an Enraf-Nonius CAD4 four-circle diffractometer using graphite monochromated MoK_α radiation (0.71073 Å) and operating in the ω-2θ mode within the range $2 < 2\theta < 50°$. An empirical absorption correction (ψ scans) was applied [28] and data reduction was performed within the WINGX [29] suite of programs. For $[Cu(dapsbz)]_2$ crystallographic data were collected on an Oxford Diffraction Gemini CCD diffractometer employing Cu-Kα radiation (1.54180 Å) and operating in the ω-scan mode. Data reduction and empirical absorption corrections (multi-scan) or analytical absorption corrections were performed with Oxford Diffraction CrysAlisPro software.

Both structures were solved by direct methods with SHELXS and refined by full-matrix least-squares analysis with SHELXL97 [30]. Non-hydrogen atoms were refined with anisotropic thermal parameters, whereas H-atoms were included at estimated positions. Drawings of the molecules were produced with ORTEP3 [31]. Ball and stick views of $[Cu(dapsbz)]_2$ and $[Ni(dapsme)]_2$ were generated with Mercury version 3.1, http://www.ccdc.cam.ac.uk/mercury/. A summary of the crystal data, structure solution and refinement parameters are given in Table 1 and selected bond lengths and angles appear in Table 2.

Table 1 Crystal and refinement data

	$[Cu(dapsbz)]_2$	$[Ni(dapsme)]_2$
Formula	$C_{50}H_{46}Cu_2N_{10}S_8$	$C_{26}H_{30}N_{10}Ni_2S_8$
f.w.	1170.53	856.50
T (K)	293	293
Crystal system	Monoclinic	Tetragonal
Space group	*C* 2/*c*	$P\,4_1\,2_1\,2$
a (Å)	17.891(4)	13.3723(6)
b (Å)	17.943(2)	
c (Å)	18.049(4)	19.712(1)
β (°)	116.87(2)	
V (Å^3)	5169(2)	3524.9(3)
Z	4	4
λ (Å)	0.71073	1.54180
ρ (g cm^{-3})	1.504	1.614
μ (mm^{-1})	1.193	6.056
$\theta_{min,max}$ (°)	1.71 to 24.97	3.99 to 60.60
F(000)	2408	1760
Meas. refl.	4693	5174
Indep. refl	4539	2531
R_{int}	0.0212	0.0415
Obs. refl.	2709	1915
R_1 (obs data), wR_2 (all data)	0.0385, 0.1090	0.0462, 0.1172
GoF	1.006	1.049
CCDC No.	992737	992738

3. Results and Discussion

Because of the presence of the thioamide (-NH-C=S) functional groups, the Schiff bases can remain either as the thione tautomer (1a) or the thiol tautomer(1b), or as a mixture of both tautomers. Previous studies [1e,1f,1g,27] have shown that, in the solid state as well as in solution, the Schiff bases remain in their thione tautomeric forms (1a). However, in solution and in the presence of nickel(II) and copper(II) salts, they convert to the thiol tautomeric forms, deprotonate and coordinate with these metal ions in their deprotonated thiolate forms. The IR spectra of both complexes lack the νNH band of the free ligands at *ca.* 3100 cm^{-1}, indicating that the deprotonated forms of the ligands are coordinated to the metal ions. X-ray crystallographic structure determination of the $[Ni(dapsme)]_2$ and $[Cu(dapsbz)]_2$ complexes (*vide infra*) unequivocally confirms that the Schiff bases are coordinated with the nickel(II) and copper(II) ions as dinegatively charged ligands. The related pentadentate thiosemicarbazones derived from 2,6-diacetylpyridine have been found to coordinate with metal ions in both the protonated thione and deprotonated thiolate forms [32-35], but the 2,6-diacetylpyridine Schiff bases of S-alkyl/aryl dithiocarbazates, despite being structurally very similar to the thiosemicarbazones, have always been found to coordinate with metal ions in their deprotonated thiolate forms [1e,1f,1g,27]. Attempts to prepare copper(II) and nickel(II) complexes of the protonated forms of these ligands have so far been unsuccessful.

3.1 Crystal structures

3.1.1 The structure of $[Cu(dapsbz)]_2$

The molecular structure of the complex, with the atom numbering scheme adopted, is shown Fig. 2 and selected bond lengths and angles are given in Table 2.

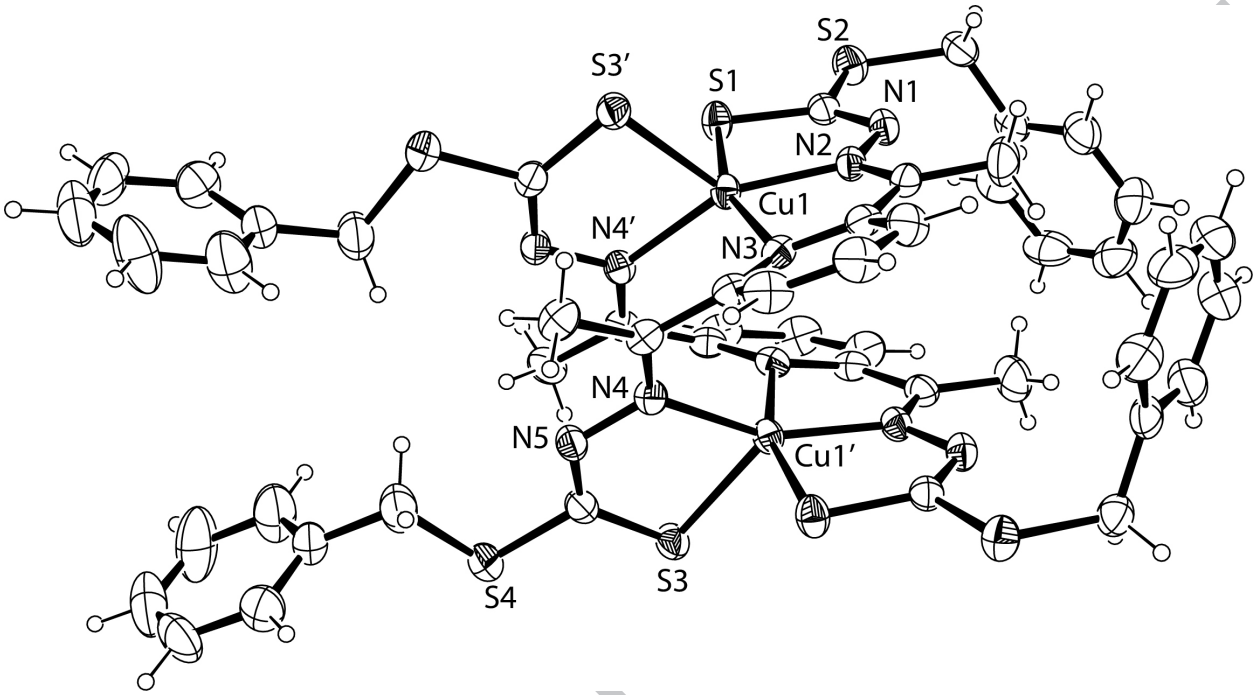


Fig. 2. ORTEP view of $[Cu(dapsbz)]_2$ (30% probability ellipsoids). The crystallographic 2-fold axis is horizontally oriented (primes denote symmetry operation $-x+2,y,-z+½$).

The structure shows that the complex is a dimeric double helicate where each copper(II) ion adopts a five-coordinate configuration. The dimer occupies a crystallographic 2-fold axis that is orthogonal to the helical axis, so both Cu ions are in identical environments. The pyridine nitrogen atom, the azomethine nitrogen atom and the thiolate sulfur atom of one ligand coordinate with a copper(II) ion and an azomethine nitrogen atom and a thiolate sulfur atom from the second ligand complete the coordination sphere of the copper(II) ion, leading to an N_3S_2 donor environment around each copper atom. Both the Schiff bases are coordinated with the

copper(II) ions in their iminothiolate forms, as supported by the C-S bond distances which are longer than those reported for free thiosemicarbazones [36] and dithiocarbazates [37]. The C-S bond distances are, however, intermediate between a C-S single bond [1.82 Å] and a C=S double bond 1.56 Å [38].

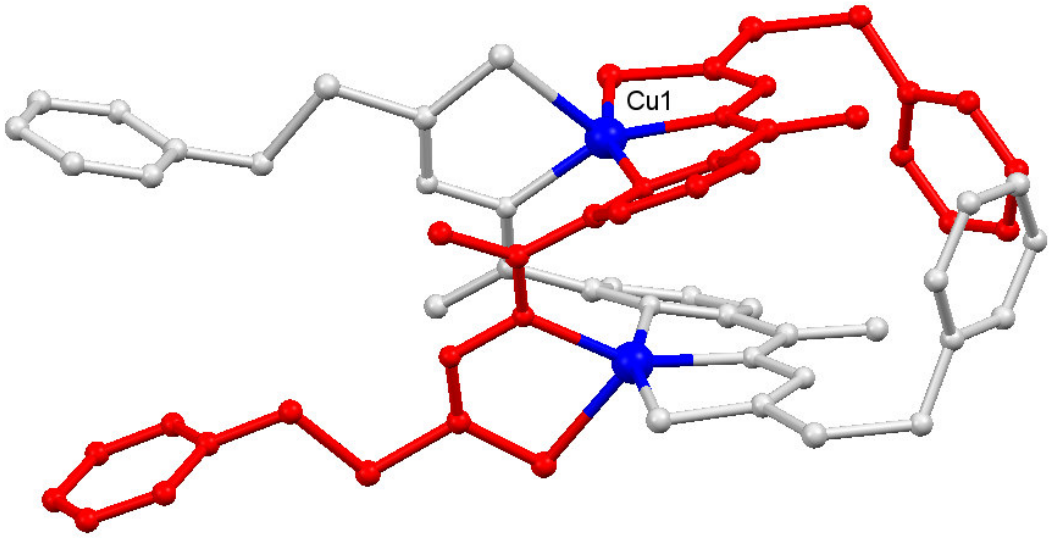


Fig. 3. Ball and stick view of $[Cu(dapsbz)]_2$ where the two symmetry related ligands are differently coloured. The two-fold axis is aligned horizontally and the Cu ions are crystallographically identical.

The double helical structure is more clearly seen in Fig. 3, where the two symmetry related $dapsbz^-$ ligands are coloured differently and the H-atoms have been removed. The Cu…Cu distance is 3.822(2) Å.

Table 2. Selected bond lengths (Å) and bond angles (°).

	$[Cu(dapsbz)]_2$	$[Ni(dapsme)]_2$
Cu1-S1 / Ni1-S1	2.289(1)	2.348(2)
Cu1-N2 / Ni1-N2	1.973(3)	1.983(5)
Cu1-N3 / Ni1-N3	2.124(3)	2.424(4)
Cu1′-N3 / Ni2-N3	–	2.331(5)
Cu1′-N4 / Ni2-N4	2.091(3)	1.999(5)
Cu1′-S3 / Ni2-S3	2.405(1)	2.364(2)
C1-S1	1.714(4)	1.718(7)
C1-N1	1.298(5)	1.301(7)
C12-N5	1.304(5)	1.316(7)
C12-S3	1.708(4)	1.690(6)
S1-Cu1-S3′ / S1-Ni-S1′	99.55(4)	102.6(1)
S1-Cu1-N2 / S1-Ni1-N2	83.2(1)	83.4(2)
S1-Cu1-N3 / S1-Ni1-N3	161.64(9)	157.9(1)
N3-Cu1-N3′ / N3-Ni-N3′	–	89.3(2)
Cu1-N3-Cu1′ / Ni1-N3-Ni2	–	88.4(2)

While coordinating with the copper(II) ions in their iminothiolate forms, the negative charges generated due to deprotonation of the ligands are delocalized across the S-C-N-N- groups, as shown by the C1-N1/C12-N5 and C1-S1/C12-S3 bond lengths which are in between those found in typical single and double bonds. The bonding of the ligands in the copper(II) complex resembles that found in the dinuclear zinc(II) complex previously reported by Akbar Ali *et al.* [1f].

The two crystallographically identical copper(II) ions adopt a five-coordinate configuration with a CuN_3S_2 coordination sphere. Since five-coordinate complexes can either adopt a square-pyramidal or a trigonal-bipyramidal geometry, the formula $\tau = (\alpha - \beta)/60$ of Addison *et al.* [39] (where α and β are the two largest coordinate angles) has been used to quantify the degree of distortion between the two extremes. Using the above formula, the τ value for the present complex is 0.03, indicating that the stereochemistry adopted by each copper(II) ion in the complex is close to square-pyramidal. However, examination of bond angle data in Table 2 indicates that most coordinate angles deviate considerably from 90° or 180°, which may be attributed to the restricted bite angles of the chelate ligand, so the geometry is far from ideal square pyramidal.

The Cu1–S1/S3, Cu1–N2/N4 and Cu1–N3 bonds agree well with those observed in other five-coordinate copper(II) complexes of NS mixed donor ligands (Table 3). An examination of the bond length data in Table 3 indicates that, despite the differences in the nature of the ligands, the copper(II)-donor atom distances in these complexes are quite similar. As expected for a square pyramidal Cu(II) complex, the axial coordinate bond (Cu1–S3′) is elongated relative to the equatorial bond (Cu1–S1) due to the pseudo Jahn-Teller effect operative on the d^9 electronic ground state [40].

Table 3 Comparison of coordinate bond distances in some approximately square-pyramidal copper(II) complexes of sulfur-nitrogen chelating agents.

Compound[a]	Cu – S_{eq}	Cu – $N_{imine.}$	Cu – $N_{py,}$ eq	Reference
$[Cu(dpksbz)Cl]_2$	2.2681(18)	1.974(5)	2.048(5)	[1h]
$[Cu(dpksme)(H_2O)]_2(NO_3)_2$	2.2787(15)	1.969(4)	2.011(4)	[1h]
$[Cu(dpksbz)(NO_3)]_2$	2.2786(9)	1.966(2)	2.026(2)	[1h]
$[Cu(dapsbz)]_2$	2.2889(13)	1.974(3)	2.091(3)	This work

3.1 .2 **The structure of $[Ni(dapsme)]_2$**

The structure of $[Ni(dapsme)]_2$ is shown in Fig. 4 and important bond lengths and angles are given in Table 2. The structure shows that the complex is again a double helical dimer. However, in this case the complex is situated in a crystallographic 2-fold axis which includes the two Ni ions; thus unlike the Cu complex discussed above, the two metal ions are not symmetry related. Another difference is that the two nickel(II) ions are six-coordinate. This is achieved by the central pyridyl N-donor (N3) bridging the two Ni ions in an unusual μ_1 mode.

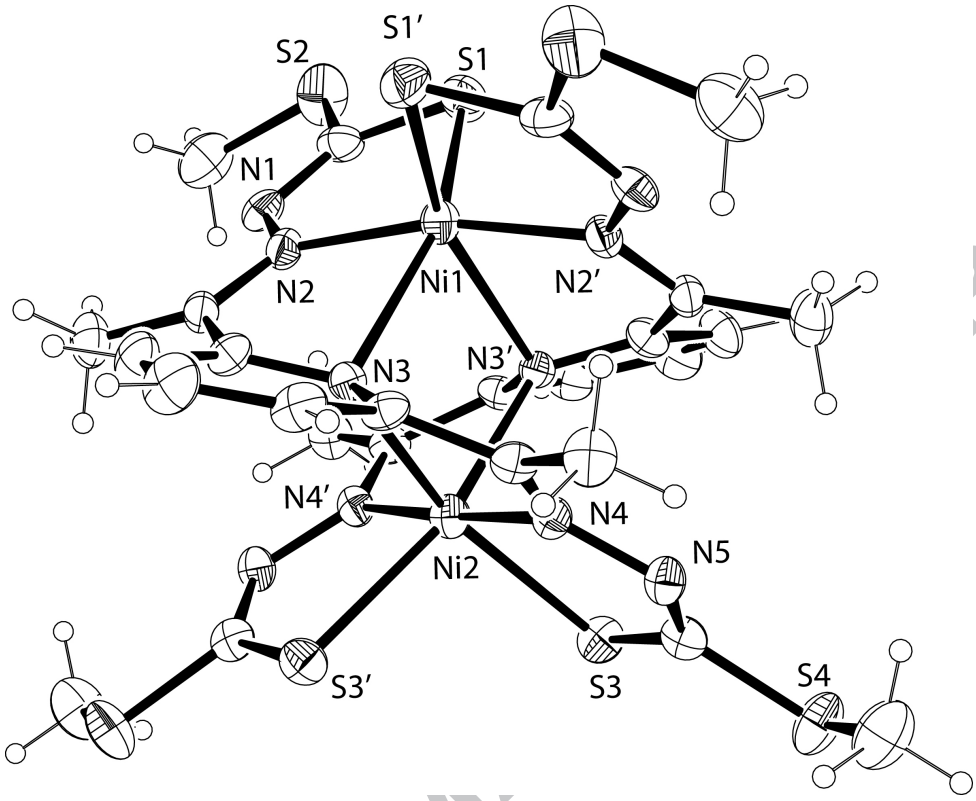


Fig. 4. ORTEP view of $[Ni(dapsme)]_2$ (30% probability ellipsoids). The crystallographic 2-fold axis is aligned vertically and includes Ni1 and Ni2. Primes denote symmetry operation y-1, *x*+1, -*z*+1.

There are less than 40 examples of this M-N_{pyr}-M′ motif in the Cambridge Structural Database that involve transition metals and the majority of these examples are supported by dinuclear double helical complexes of d^{10} metals (Zn(II), Hg(II), Cu(I) and Ag(I)) bearing extended multidentate ligand systems. For some examples see [41]. Examples of Ni(II) complexes bearing this bridging pyridyl motif are much less common [1e,42]. It should be mentioned that the pyridyl coordinate bonds around each Ni(II) center in $[Ni(dapsme)]_2$ are very weak (Ni1/2-N3 > 2.3 Å), and are at the limit of what would be considered a genuine coordinate bond (*cf.* Ni1-N2 and Ni2-N5 ~1.99 Å, Table 2).

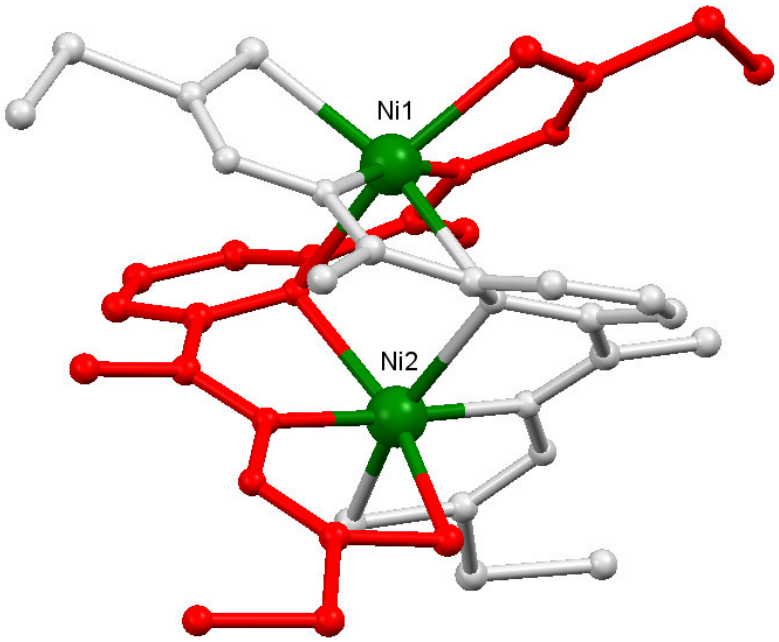


Fig. 5. Ball and stick representation of the structure of $[Ni(dapsme)]_2$ with the crystallographically equivalent ligands shown in different colours. The 2-fold axis is oriented vertically.

In Fig. 5 the double helical structure is portrayed without H-atoms and again with the symmetry related ligands in different colours. Note that the 2-fold axis in this case is parallel with the helical axis (and not orthogonal as for the Cu complex discussed earlier). The Ni…Ni distance in this case is 3.316(2) Å, which is much shorter than found in $[Cu(dapsbz)]_2$ (3.822(2) Å) due to the bridging pyridyl N-donor. From the bond lengths in Table 2, Ni2 is slightly closer to the bridging donor N3 than Ni1, but apart from this the two coordination environments are very similar. Each nickel(II) ion is in a distorted octahedral geometry. All of the angles within

the chelate rings are well away from 90 or 180° (Table 2), but those unrestrained by chelation are closer to ideal [N4-Ni2-N4′ 177.1(3)^{o}, N3-Ni1-N3′ 89.3(2), S1-Ni1-N3′ 87.92(12) and N3-Ni2-N3′ 93.9(3)^{o}]. A similar distorted octahedral geometry was also observed for the related dimeric $[Ni(dapsbz)]_2$ complex [1e] and the bond lengths are comparable.

3.2 **Characterization of the complexes**

The molar conductance values of both complexes in dmso are less than 10.0 ohm^{-1} cm^2 mol^{-1}, indicating that they are essentially non-electrolytes in this solvent, supporting the fact that the ligands are coordinated with the nickel(II) and copper(II) ions in their deprotonated thiolate forms. The IR spectra of the nickel(II) and copper(II) complexes, when compared with those of the free ligands, show that the ν_{NH} bands of the free ligands at *ca*. 3176 cm^{-1} are absent in the spectra of the complexes, supporting deprotonation of the ligands during coordination with the metal ions. The $\nu_{C=N}$ and ν_{N-N} bands of the free ligand H_2dapsme appear at 1617 and 1050 cm^{-1}, respectively. These bands shift to 1593 and 1082 cm^{-1}, respectively in the IR spectrum of $[Ni(dapsme)]_2$, indicating coordination *via* the azomethine nitrogen atom [1c]. The electronic spectrum of the nickel(II) complex in the 1000-200 nm range shows a *d-d* band as a shoulder at *ca.* 640 nm, a $S\rightarrow Ni^{II}$ charge transfer band at 420 nm and an intra-ligand band at 348 nm. Six-coordinated nickel(II) complexes are expected to exhibit three bands in the visible and near IR region, corresponding to the transitions, $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{1g}$(P) transitions. The shoulder at 640 nm in the electronic spectrum of $[Ni(dapsme)]_2$ may be assigned to the $^3A_{2g} \rightarrow {}^3T_{1g}$(P) transition. The first band corresponding to the transition $^3A_{2g} \rightarrow {}^3T_{2g}$ in the electronic spectrum of six-coordinate nickel(II) complexes generally occurs in the near IR region. This band could not be observed in the spectrum of $[Ni(dapsme)]_2$ because of the

limitation of the spectrophotometer used. The third band corresponding to the transition $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ also could not be observed because it is obscured by the intrusion of an intense LMCT band extending up to the visible portion of the spectrum.

The IR spectrum of the $[Cu(dapsbz)]_2$ complex shows the azomethine νC=N band at 1571 cm^{-1} and the νN-N band at 1126 cm^{-1}, supporting coordination *via* the azomethine nitrogen atoms [1c]. The νCSS band of the free ligand H_2dapsbz, at 957 cm^{-1}, is split into two components in the IR spectrum of the copper(II) complex, which is evidence that coordination takes place *via* one of the sulfur atoms [43]. The electronic spectrum of $[Cu(dapsbz)]_2$ is dominated by an intense ligand-to-metal charge transfer band, making assignments of the *d-d* bands difficult. However, a broad band with a maximum at *ca.* 600 nm may be assigned to a *d-d* band of copper(II). The shoulder at *ca.* 430 nm and a band at 346 nm may be assigned to the $S \rightarrow Cu^{II}$ charge-transfer and an intra-ligand band, respectively.

4. Conclusion

The 2,6-diacetyl pyridine Schiff bases of S-methyl- and S-benzyldithiocarbazates act as dinegatively charged dinucleating ligands, yielding dimeric double helical nickel(II) and copper(II) complexes. In the nickel(II) complex $[Ni(dapsme)]_2$, the Schiff base H_2dapsme utilizes its pyridine nitrogen atom as a bridging donor atom and the azomethine and thiolate sulfur atoms as other donor atoms, leading to NiN_4S_2 coordination cores. The Schiff base H_2dapsbz, on the other hand, forms a helical dimeric copper(II) complex without any shared donor atoms, in which the bonding of the ligands with the copper(II) ions occurs *via* the pyridine

nitrogen, azomethine nitrogen and thiolate sulfur atoms, each copper(II) ion in the dimer being in an N_3S_2 donor environment.

5. Supplementary data

CCDC Nos. 992737 and 992738 contain the supplementary crystallographic data for $[Cu(dapsbz)]_2$ and $[Ni(dapsme)]_2$, respectively. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)-1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk

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5. References

[1] (a) A.H. Mirza, M.H.S.A. Hamid, S. Aripin, M.R. Karim, Md. Arifuzzaman, M. Akbar Ali, P.V. Bernhardt, Polyhedron 74 (2014) 16;

(b) M. Akbar Ali, P.V. Bernhardt, M.A.H. Brax, J. England, A.J. Farlow, G.R. Hanson, L.L. Yeng, A.H. Mirza, K. Wieghardt, Inorg. Chem. 52 (2013) 1650;

(c) M. Akbar Ali, A.H. Mirza, W.Y. Ting, M.H.S.A. Hamid, P.V. Bernhardt, R.J. Butcher, Polyhedron 48 (2012) 167;

(d) M. Akbar Ali, A.H. Mirza, C.Y. Yee, H. Rahgeni, P.V. Bernhardt, Polyhedron 30 (2011) 542;

(e) M. Akbar Ali, A.H. Mirza, R.J. Butcher, M.T.H. Tarafder, M.A.Ali, Inorg. Chim. Acta 320 (2001) 1;

(f) M. Akbar Ali, A.H. Mirza, C.W. Voo, A.L. Tan, P.V. Bernhardt, Polyhedron 22 (2003) 3433;

(g) M. Akbar Ali, A.H. Mirza, L.K. Wei, P.V. Bernhardt, O. Atchade, X. Song, G. Eng, L. May, J. Coord. Chem. 63 (2010) 1194;

(h) M. Akbar Ali, A.H. Mirza, R.J. Butcher, P.V. Bernhardt, M.R. Karim, Polyhedron 30 (2011) 1478;

(i) M. Akbar Ali, A.H. Mirza, L.K. Wei, A.L. Tan, P.V. Bernhardt, Polyhedron 23 (2004) 2037

[2] M.T. Basha, J.D. Chartres, N. Pantarat, M. Akbar Ali, A.H. Mirza, D.S. Kalinowski, D.R. Richardson , P.V. Bernhardt, Dalton Trans. 41 (2012) 6536.

[3] T- J. Khoo, M.K.B. Break, K.A. Crouse, M. Ibrahim, M. Tahir, A.M. Ali, A.R. Cowley, D.J. Watkin, M.T.H. Tarafder, Inorg. Chim. Acta 413 (2014) 68.

[4] N.K. Singh, M.K. Bharty, S.K. Kushawaha, U.P. Singh, P. Tyagi, Polyhedron, 29 (2010), 1902.

[5] M.R. Maurya, D.C. Antony, S. Gopinathan, C. Gopinathan, Bull. Chem. Soc. Jpn. 16 (1995) 554.

[6] P. Bera, C.H. Kim, S. Il Seok, Inorg. Chim. Acta 362 (2009) 2603.

[7] A. Nunez-Montenegro, R. Carballo, E.M. Vazquez-Lopez, Polyhedron 27 (2008) 2867.

[8] M. Yazdanbakhsh, R. Takjooa, Struct. Chem. 19(2008) 895.

[9] Y. Tian, C.Y. Duan, C. Zhao, X. You, T.C.W. Mak, Z.Y. Zhang, Inorg. Chem. 36 (1997) 1247.

[10] Z A. Abu-Raqabah, G. Davies, M.A. El-Sayed, A.El-. Toukhy, S.N. Shaikh, J. Zubieta, Inorg. Chim. Acta 193 (1992) 43.

[11] Z.H. Liu, C.Y. Duan, J. Hu, Inorg. Chem. 38 (1999) 1719.

[12] C.Y. Duan, X.Z. You, Chem. Lett. Jpn. 10 (1999) 1063.

[13] Y. Tian, C.Y. Duan, X. You, T.C.W. Mak, Q. Luo, J. Zhou, Transition Met. Chem. 23 (1998).

[14] M. Akbar Ali, A.H. Mirza, R.J. Butcher, M.T.H. Tarafder, Tan Boon Keat, A.Manaf Ali, J. Inorg. Biochem. 92 (2002) 141.

[15] M.E. Hossain, M.N. Alam, J. Begum, M. Akbar Ali, M. Nazimuddin, F.E. Smith, R.C. Hynes, Inorg. Chim. Acta 249 (1996) 207.

[16] T.B.S.A. Ravoof, K.A. Crouse, M.I.M. Thahir, A.R. Cowley, M. Akbar Ali, 23 (2004) 2491.

[17] M. Das, S.E. Livingstone, Br. J. Cancer 37 (1978) 101.

[18] A. Saxena, J.K. Koacher, J.P. Tandon, Antibact. Antifung. Agents 9 (1981) 435.

[19] A. Saxena, J.K. Koacher, J.P. Tandon, J. Toxicology Environ. Health 15 (1985) 503

[20] P.I. da S. Maia, A.G. de A. Fernandes, J.J.N. Silva, A.D. Andricopulo, S.S. Lemos, E.S. Lang, U.A. Abram, V. M. Deflon, J. Inorg. Biochem. 104 (2010) 1276.

[21] A. Boschi, A. Massi, L. Uccelli, M. Pasquali, A. Duatti, Nucl. Med. Biol. 37 (2010) 927.

[22] F.R. Pavan, Eur. J. Med. Chem. 45 (2010) 1898.

[23] A.B. Beshir, S.K. Guchhait, J.A. Gasco´n, G. Fenteany, Bioorg. Med. Chem. Lett. 18 (2008) 498.

[24] M.A.F.A. Manan, M.I.M. Tahir, K.A. Crouse, R. Rosli, F.N.-F. How, D.J. Watkin, J. Chem. Crystallogr. 41 (2011) 1866.

[25] M.R. Maurya, S. Khuran,Shailendra, A. Azam, W. Zhang, D. Rehde, Eur. J. Inorg. Chem. 2003 (2003) 1966.

[26] P. K. Sasmal, A.K. Patra, A.R. Chakravarty, J. Inorg. Biochem, 102 (2008)1463.

[27] S.M.M.H. Majumder, M. Akbar Ali, F.E. Smith, M.A.U. Mridha, Polyhedron 7 (1988) 2183.

[28] A.C.T. North, D.C. Phillips, F.S. Mathews, Acta. Crystallogr. Sect A, 24 (1968) 351.

[29] L.J. Farrugia, J. Appl. Cryst. 32 (1999) 837.

[30] G. M. Sheldrick, Acta Cryst. Sect. A, 64 (2008) 112.

[31] L. J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.

[32] R. Pedrido, A.M. Gonzalez-Noya, M.J. Romero, M. Martınez-Calvo, M.V. Lopez, E. Gomez-Forneas, G. Zaragoza, M, R. Bermejo, Dalton Trans. (2008) 6776.

[33] G. Dessy, V. Fares, Cryst. Struct. Commun. 10 (1981) 1025.

[34] A. Bino, N. Cohen, Inorg. Chim. Acta 210 (1993) 11.

[35] M. Mohan, P. Sharma, M. Kumar, N.K. Jha, Inorg. Chim. Acta 125 (1986) 91.

[36] (a) M. Serda, J.G. Malecki, A. Mrozek-Wilczkiewicz, R. Musiol, J. Polanski, J. Mol. Struct. 1037 (2013) 63;

(b) R. Pedrido, A.M. Gonzalez-Noya, M.J. Romero, M. Martinez-Calvo, M.V. Lopez, E. Gomez-Forneas, G. Zaragoza, R. Bermejo, Dalton Trans. (2008) 6776;

(c) E. Labisbal, K.D. Haslow, A. Sousa-Pedrares, J. Valdes-Martinez, S. Hernandez-Ortega, D.X. West, Polyhedron 22 (2003) 2831;

(d) M. Joseph, M. Kuriakose, M.R.P. Kurup, E. Suresh, A. Kishore, S.G. Bhat, Polyhedron 25 (2006) 61;

(e) T.S. Lobana, S. Khanna, R.J. Butcher, A.D. Hunter,M. Zeller, Polyhedron, 25 (2006) 2755.

[37] (a) M. Haniti, S.A. Hamid, M. Akbar Ali, A.H. Mirza, P.V. Bernhardt, B. Moubaraki, K. S. Murray, Inorg. Chim. Acta 362(2009) 3648.

(b) M. Akbar Ali, H.J. Hj, A. Bakar, A.H. Mirza, S.J. Smith, L.R.Gahan, P.V. Bernhardt, Polyhedron 27 (2008) 71.

(c) M. Akbar Ali, A.H. Mirza, R.J. Fereday, R.J. Butcher, J.M. Fuller, S. Drew, L.R. Gahan, G.R. Hanson, B. Moubaraki, K.S. Murray, Inorg. Chim. Acta 358 (2005) 3937;

[38] L.E. Sutton (ed.) (1965), Tables of Interatomic Distances and Configuration in Molecules and Ions. "Supplement 1956–1959, Special publication No. 18, London, Chemical Society.UK:

[39] A. Addison, T. Rao, J. Reedjik, J. Van Rijn, G. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.

[40] B. Murphy, B. Hathaway, Coord. Chem. Rev. 243 (2003) 237.

[41] (a) C.Piguet, G.Bernardinelli, A.F.Williams, Inorg. Chem. 28 (1989) 2920;

(b) G. Baum, E.C. Constable, D. Fenske, C.E. Housecroft, T. Kulke, Chem. Commun. (1998) 2659;

(c) C. Lorenzini, C. Pelizzi, G. Pelizzi, G. Predieri, J. Chem. Soc., Dalton Trans. (1983) 2155;

(d) M. Tang, L. Li, Y. Fan, Angew. Chem., Int. Ed. 44 (2005) 6067;

(e) E.C. Constable, A.J. Edwards, M.J. Hannon, P.R. Raithby, Chem. Commun. (1994) 1991;

(f) M.J. Hannon, C.L. Painting, E.A. Plummer, L.J. Childs, N.W. Alcock, Chem.-Eur. J., 8 (2002) 2225.

[42] R. Pedrido, M.V. Lopez, L. Sorace, A.M. Gonzalez-Noya, M. Cwiklinska, V. Suarez-Gomez, G.Zaragoza, M.R.Bermejo, Chem.Commun. 46 (2010) 4797.

[43] M. Akbar Ali, S.E. Livingstone, D.J. Phillips, Inorg. Chim. Acta 5 (1971) 119.

Graphical abstract

Dimeric nickel(II) and copper(II) complexes of the pentadentate N_3S_2 chelating agents derived from S-alkyl/aryl esters of dithiocarbazic acid Aminul H. Mirza, Mohammad Akbar Ali, Paul V. Bernhardt	Helical dimeric nickel(II) and copper(II) complexes have been synthesized and structurally characterized. Each copper(II) ion in the dimeric copper complex is five-coordinate whereas the nickel(II) ions in the dimeric nickel complex adopt a distorted octahedral geometry.